IV.D.2 Hydrogen Storage in Metal-Organic Frameworks

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Contract Number: DE-FG36-05GO15001

Project Start Date: May 1, 2005
Project End Date: April 30, 2009

Objectives

- Utilize new concepts for increased surface area
- Implement strategies for higher adsorption energy
- Develop strategies for increased hydrogen density in metal-organic frameworks (MOFs)

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(C) Efficiency
(E) Charging/Discharging Rates
(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project is conducting fundamental studies of MOFs. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Volumetric density: 45 g/L
- Gravimetric density: 60 mg/g

Accomplishments

- Collected H_2 adsorption data for a series of MOF materials at 77 K. The results indicate that open metal sites and catenation of frameworks improve interaction between H_2 and adsorbents.
- Independent measurements of H_2 uptake in MOF-177 are performed by volumetric and gravimetric methods to verify their saturation H_2 uptake.
- From H_2 adsorption results, absolute adsorbed amounts of H_2 in the MOF materials are estimated.
- Complete uptake and release of H_2 between 2 and 53 bar is achieved within 5 minutes at 77 K, which is shown by cycling curve for IRMOF-62.

Introduction

Conventional storage of large amounts of hydrogen in its molecular form is difficult and expensive because it requires employing either extremely high pressure as a gas or very low temperatures as a liquid. In contrast to this, MOFs exhibit the highest hydrogen uptake of any porous materials and clearly show that in principle the DOE targets can be achieved at 77 K. For the implementation of room temperature hydrogen storage in MOF materials, design of a new class of porous solids, which is based on the understanding hydrogen physisorption mechanism in MOFs, is necessary. We are therefore undertaking efforts to discover highly porous materials having a strong affinity with hydrogen.

Approach

Hydrogen uptake capacity substantially is influenced by adsorption enthalpy (ΔH) and pore volume (V_p) of the materials. The value of ΔH and V_p are usually evaluated by H_2 isotherms at very low pressure and the high pressure region, respectively. Therefore, sometimes lack of understanding of H_2 physisorption confused us, which is one of the problems to make strategies for meeting the DOE target. In this year, we tested a series of MOFs possessing various functionalities, pore structures, and surface areas to promote better understanding for H_2 adsorption behaviors.

For evaluation of high pressure H_2 uptake capacity with high accuracy, although well-characterized standard materials should be useful, only limited

materials show high H_2 uptake capacity even at 77 K and high pressure region. It is obvious that benchmark materials are important because the field of hydrogen storage has often suffered from reports of high H_2 uptake which were later found to be erroneous. As our DOE sponsor has advised that independent measurements of H_2 uptake should be performed at a DOE-approved facility (Southwest Research Institute), we have independently measured H_2 uptake in MOF-177. In addition to the verification, we estimated an absolute adsorbed amount of H_2 in the MOF materials, which value would represent the total amount of H_2 in the experimental system.

Results

Metal-oxide secondary building units (SBUs) and the organic carboxylate links of the MOFs were prepared (Figure 1). The isoreticular MOF (IRMOF) series, IRMOF-1, -13, and -62, are derived from the basic zinc acetate unit, $Zn_4O(CO_2)_6$, with linear ditopic carboxylates. MOF-324 whose connectivity is a simple cubic system is constructed from a Zn cluster and ditopic link. MOF-199 and MOF-505 are composed of the $Cu_2(CO_2)_4$ paddle-wheel SBU linked by tritopic and tetratopic carboxylates.

Low Pressure Hydrogen Adsorption in MOFs

To compare the effects of link functionalization and length, H_2 isotherms are measured at 77 K for non-catenated IRMOFs -1, -8 and MOF-324. These results are illustrated in Figure 2. Both IRMOFs, whose link lengths are different, adsorb comparable amounts of H_2 (13–15 mg/g) at 1 bar. Although IRMOF-8 shows higher H_2 uptake than IRMOF-1 due to large pores, their curvatures are similar to each other. This indicates that interaction between H_2 and adsorbents are essentially not so different. In contrast to this, MOF-324 having a similar cubic framework, shows good performance for H_2 adsorption (21 mg/g). Considering that MOF-324 does not have strong binding sites such as open metal sites, it is unlikely that large parts of H_2 molecules are physisorbed on organic groups. It is probable that the effective H_2 uptake is attributed to the small pore diameter (7.6 Å) which is roughly three times larger than the kinetic diameter of dihydrogen. Also, two nitrogen atoms in the PyC link may help with the polarization of adsorbent, leading to an improvement of adsorption enthalpy.

For reducing pore dimensions, interpenetration of two or more frameworks should be an effective strategy. The interpenetration may reduce accessible pore volume of materials, especially when a second framework is placed in the middle of the first one. However, it can be said that interwoven structures can keep enough pore volume to store hydrogen molecules, aside from another effect that structural reinforcement may prevent framework collapse. H_2 isotherms for IRMOFs -13 and -62 whose catenation numbers are 2 and 4, respectively, are overlaid in Figure 2. These interpenetrating IRMOFs outperform IRMOF-1 across the entire range of pressure examined. When these results are normalized per $Zn_4O(link)_3$ formula unit, the uptakes at 1 bar are nearly double that of IRMOF-1. Such H_2 uptake behavior at the low-pressure region indicates that the adsorption enthalpy for catenated IRMOFs is enhanced because of a large Henry's law constant (isotherm slope as P→0).

To improve further both the H_2 uptake capacity and adsorption enthalpy in MOFs, it is necessary to present adsorptive sites with greater interaction potential while maintaining a large total pore volume of appropriate pore dimensions. As expected, MOFs -199 and -505

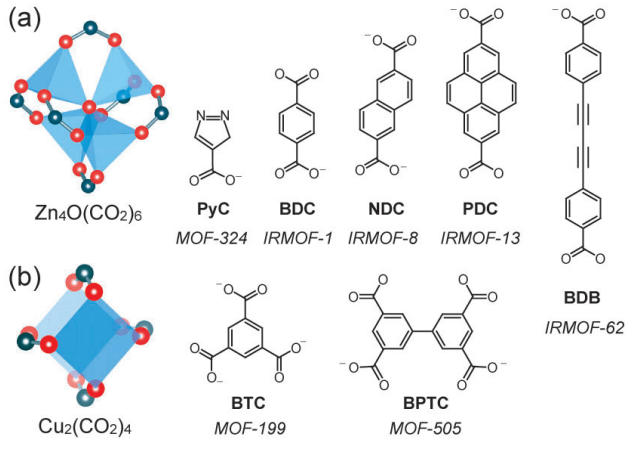

FIGURE 1. (a) $Zn_4O(CO_2)_6$-based MOFs in italics derived from the link in parentheses: IRMOF-1 (BDC), IRMOF-8 (NDC), IRMOF-13 (PDC), IRMOF-62 (BDB), and MOF-324 (PyC); (b) MOF-199 and -505, $Cu_2(CO_2)_4$-based MOFs with BTC and BPTC, respectively.

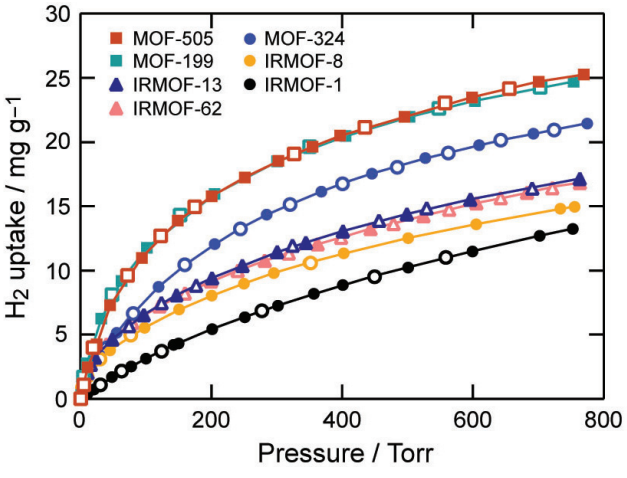

FIGURE 2. H_2 adsorption isotherms for MOFs measured at 77 K in gravimetric units. Data for IRMOF-1 is shown for comparison. Adsorption data are shown as closed circles, desorption data as open circles, and connecting traces are guides for eyes.

possessing open metal sites (Cu paddle wheel units) show a significant improvement over the other MOFs without them. From the large slopes of isotherms at the low-pressure region, it is apparent that these materials demonstrate much stronger binding of H_2 due to open Cu^{2+} sites. The amounts adsorbed in gravimetric unit for these MOFs are approximately double that of IRMOF-1.

Estimation of the Adsorption Enthalpy For MOF-324 and IRMOF-62, coverage dependencies of ΔH for H_2 were calculated from the fits of their 77 and 87 K isotherms. The ΔH at zero coverage for IRMOF-62 is estimated to be 7.4 kJ/mol and shows gradual decrement to 5.0 at 11 mg/g of surface coverage. The initial value is higher than those of MOFs -199 and -505 (6.5 – 7.0 kJ/mol). Since ΔH does not always reflect the interaction with strong binding sites, we cannot conclude that catenation of the frameworks leads to stronger interaction sites. Considering small ΔH for IRMOF-1 (4.8 kJ/mol), the improvement of ΔH is probably attributed to the effective pore diameter (5.2 Å) of IRMOF-62.

In the case of MOF-324, ΔH value is not influenced with the surface coverage comparing to IRMOF-62; 6.2 kJ mol at the zero coverage decreases to 5.6 kJ/mol at 15 mg/g of surface coverage. Although the results indicate that MOF-324 does not have a very strong hydrogen binding site, the constant ΔH value for the isotherms in accordance with Henry's law is a desirable property for H_2 storage materials. In such a scenario, H_2 storage capacity should not be influenced by surface coverage, leading to a large amount of available H_2 as the low-pressure limit of the delivery system is approached.

Independent Verification of High Pressure H_2 Adsorption in MOF-177 High-pressure hydrogen uptake properties for MOF-177 were evaluated by use of volumetric and gravimetric techniques. Isotherms acquired volumetrically are illustrated in Figure 3. These isotherms saturate at near 60 bar with maximum surface excess amounts of 75 mg/g. The profiles are similar to the data which we have reported previously [1]. Gravimetric measurement provides a similar profile as the volumetric isotherm measured at 77 K. The reversible isotherm indicates that H_2 is physisorbed even in the high-pressure region. After buoyancy correction, the uptake (surface excess amount) is 73 mg/g at a saturation pressure of approximately 50 bar.

Absolute adsorbed amounts of H_2 are calculated using the total pore volume (V_p) of MOF-177 and H_2 density at the given pressure (ρ_{bulk}); (total H_2 uptake) = (surface excess mass) + $\rho_{bulk} V_p$. Estimated absolute adsorbed amount is 113 mg/g, which corresponds to 48.3 g/L. Since the absolute adsorbed amount cannot be measured experimentally, it is not possible to confirm whether or not this value is reasonable. Therefore, we compared the absolute H_2 uptake with N_2 adsorption data which were taken at 77 K. In contrast to the difference in gravimetric uptake, the volumes of adsorbed gases between N_2 and H_2 are quite similar (1,200 and 1,270 cm^3/g, respectively). Consequently, the number of adsorbed N_2 and H_2 molecules (61 and 65 adsorbates, respectively) in the formula unit is almost the same. This clearly demonstrates that the micropores in MOF-177 are in large part occupied by H_2 molecules in the high-pressure region.

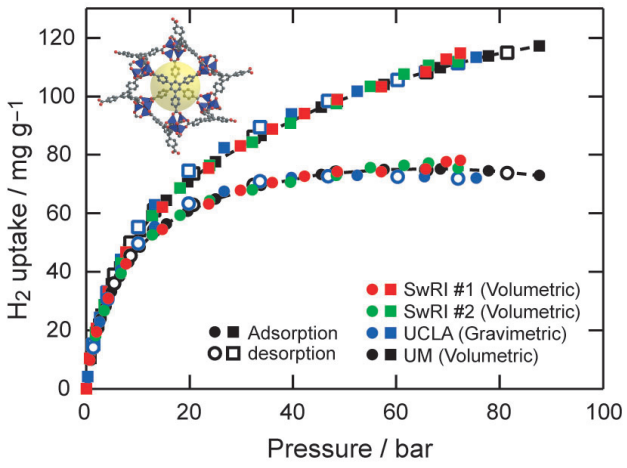

FIGURE 3. High-pressure H_2 isotherms for MOF-177 taken by volumetric (red and green circles) and gravimetric methods (blue circles). As a reference, volumetric data in Ref. 1 are shown as black circles. Filled and open symbols represent adsorption and desorption branches, respectively. Square symbols which are absolute adsorbed amounts are obtained (see text). Connecting traces are guides for eyes. Inset: crystal structure of MOF-177.

Saturation Uptakes of H_2 in MOFs Figure 4 shows the H_2 adsorption isotherms for IRMOF-62 and MOF-324 up to 80 bar at 77 K where saturation binding of H_2 is achieved. As a reference, the isotherm for MOF-177 is also overlaid. As expected by low pressure H_2 uptake behaviors, IRMOF-62 and MOF-324 show steep uptake of H_2 below 10 bar, which is in sharp contrast to MOF-177. Since H_2 uptake capacity depends on total pore volume, maximum uptakes (surface excess masses) of H_2 for IRMOF-62 and MOF-324 (49 and 33 mg/g) are lower than that of MOF-177.

From the viewpoint of H_2 storage, since the total amount that a material can store is more relevant to use for hydrogen as a fuel, absolute adsorbed amounts were estimated as described before. The maximum hydrogen uptake for IRMOF-62 is 68 mg/g at 75 bar, and corresponding volumetric uptake is 47 g/L. It should be noted that absolute H_2 uptake in IRMOF-62 (volumetric unit) is larger than that in MOF-177 up to 60 bar. This clearly demonstrates that the interpenetration enhances hydrogen uptake even in the high pressure region. Taking into account the fact that large pore volume is preferable to large gravimetric hydrogen uptake, it can

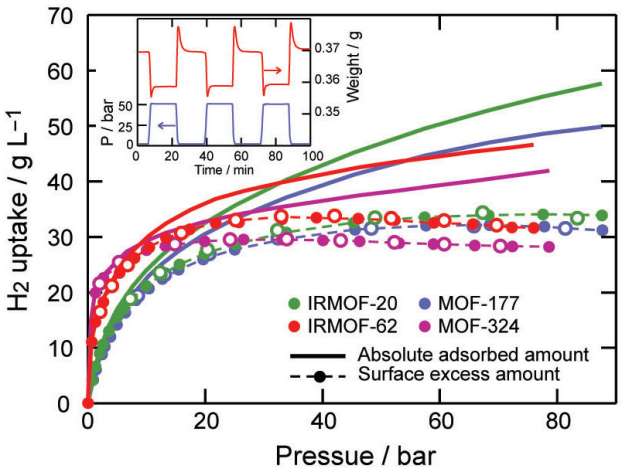

FIGURE 4. High-pressure H_2 isotherms for activated materials measured at 77 K in volumetric units (g/L). Estimated absolute adsorbed amounts are shown as lines. Inset: kinetic profile for IRMOF-62 at 77 K.

be said that desirable material should have intricate reticular to reduce dead volume.

In our annual report last year, we have only reported surface excess masses for a series of MOFs. Here we recalculated the absolute H_2 uptake for them. Surprisingly, volumetric uptake for IRMOF-20 reaches 58 g/L at 90 bar at 77 K. This is obviously one of the highest performances among the porous solids, and the value is well within the realm of the 2010 DOE "system" target of 45 g/L.

Kinetic Profile Time course profile of adsorption and successive desorption process were also recorded to illustrate their reversible and fast hydrogen uptake (and release). The red curve in inset of Figure 4 shows weight change induced by pressure change (2–53 bar). The time course profile clearly shows that adsorption and desorption processes are completed within 2-5 min even though a large pressure change was applied to the experimental system. This finding is in accordance with our consideration that hydrogen molecules are physisorbed in IRMOFs. Also, it is clear that the interpenetration does not disturb fast gas diffusion in micropores.

Conclusions and Future Directions

Highly interpenetrated material (IRMOF-62) shows good volumetric H_2 uptake as well as fast kinetic property. The result implies that decrement of dead volume (e.g. center of the pore) should be important to improve volumetric uptake. However, both large pore volume and high surface area substantially play a key role for the theoretical maximum H_2 uptake. In the future, based on our presented strategies [2], we will design a means of increasing the uptake at room temperature.

- Impregnation of metals in MOF-177 for implementation of strong binding sites.
- Inelastic neutron scattering studies to gain information on the specifics of H_2 binding in MOF-74 having large metal/organic link ratio.
- Begin testing at room temperature.

Special Recognitions & Awards/Patents Issued

1. The 2007 DOE Hydrogen Program R&D Award.

2. The 2007 Certificate of Appreciation for Outstanding Contributions given by Council of Scientific Society Presidents.

3. The 2006 Herbert Newby McCoy Award, UCLA.

4. Dean's Recognition Award at the College of Letters and Science, UCLA.

FY 2007 Publications/Presentations

1. *Independent Verification of the Saturation Hydrogen Uptake in MOF-177 and Establishment of a Benchmark for Hydrogen Adsorption in Metal-Organic Frameworks*, H. Furukawa, M. A. Miller, O. M. Yaghi, *J. Mater. Chem.* **2007**, *17*, 3197 - 3204.

2. *Hydrogen Storage and Carbon Dioxide Capture in Molecular Organic Frameworks*, O. M. Yaghi, Gordon Research Conferences, Ventura, CA, January 2007.

3. *Pores without Walls for Clean Energy,* O. M. Yaghi, 2007 ACS Spring National Meeting, Chicago, IL, March 2007.

4. *Hydrogen Storage in Metal-Organic Frameworks*, O. M. Yaghi, APS National Spring Meeting, Denver, CO, March 2007.

5. *Metal-Organic and Covalent Organic Frameworks (MOFs and COFs) as Adsorbents for Environmentally Significant Gases (H_2, CO_2, and CH_4)*, H. Furukawa, H. M. El-Kaderi, K. S. Park, J. R. Hunt, J. L. Mendoza-Cortés, A. P. Côté, O. M. Yaghi, 2007 ACS Spring National Meeting, Chicago, IL, March 2007.

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2. J. L. C. Roswell and O. M. Yaghi, *Angew. Chem. Int. Ed.*, **2005**, *44*, 4670.